

Heterogeneous Electron Transfer Studies on the Reduction of Some Pyridinium Cations: Substituents and the Inner-Reorganization Energy

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(Received on 31st October 2009, accepted in revised form 23rd June 2010)

Summary: Standard heterogeneous electron transfer rate constant k° for some important pyridinium model compounds: *N*-methyl- α -picolinium⁺, *N*-(2,4-dinitrophenyl)-4-(4'-pyridyl) pyridinium⁺, *N*-(phenyl)-4-(4'-pyridyl) pyridinium⁺, *N*-(cyanophenyl)-4-(4'-pyridyl) pyridinium⁺ and *N*-(2, 4-dinitrophenyl) pyridinium chlorides as well as 1-1' dimethyl 4-4'-bipyridinium (methyl viologen), were determined using cyclic voltammetric technique. Methods of Nicholson and Gileadi were used. k° were computed using various forms of Marcus equations. It was found that the simple Marcus equation gave much higher values of k° ; while the precursor equilibrium-model gave better agreement with the experimental results. In all these cases an adiabatic electron transfer was assumed. It was inferred that the general practice of omitting λ_i , the inner reorganization energy, can not be accepted in the present case: *when strong electron withdrawing group nitro-, cyano-, carbomethoxy- etc. are the substituents near the reaction site, λ_i should not be ignored.*

Introduction

Prologue

Pyridinium and bipyridinium compounds have been extensively studied [1-11]. A class of bipyridinium salt called viologens has been subject to various investigations [1-11], whereas pyridinium (mono-cation) compounds have relevance to biochemical reactions in NADH and NADPH [1-2]. Also, methyl viologen and *p*-cyonophenyl-4-(4'-Pyridyl) pyridinium salts showed toxicity towards cancer cells, [12]. Viologens and pyridinium salts had been studied for their electrochemical, electrochromic and nonlinear chromic properties [7-9]. Hence their redox and electron transfer kinetics studies are of interest.

While the heterogeneous electron transfer rate constants (k°) for bipyridinium compounds have been reported before and attempts have been made to analyze k° data through Marcus theory [5, 13], much less information regarding k° of mono-pyridinium-compounds is available in literature [14]. Thus (mono-) pyridinium compounds seem suitable and interesting targets for such studies: experimental determination of k° and their analysis through Marcus equation. There was another reason for determining, investigating and analyzing k° of pyridinium compounds that λ_i , the inner organization energy, of some pyridinium compounds, like that of stilbenes, were found to constitute 20% to 50% of total reorganization energy [15].

Marcus equation for k° has two parts (eq (1)) [16], a pre-exponential term A (dimension cm/s) and the other, exponential dimensionless term containing $\Delta G^* / RT$

$$k^\circ = A \exp [-\Delta G^* / RT] \quad (1)$$

ΔG^* contains outer-, (λ_o), as well as inner-, (λ_i), reorganization energy. Research workers, generally, tend to omit the latter (λ_i) [5,19-22], particularly for electron transfer to organic compounds [23]. At the same time Evans [24] alerted research workers against the tradition of neglecting λ_i .

The pre-exponential term A in eq.(1) has been shown to contain a term transmission coefficient (κ_{el}) which determines the "adiabaticity" of electron transfer. In the collision frequency and precursor models κ_{el} is generally taken to be unity. And this has been a general practice. However, there may not be *a priori* reason to assume $\kappa_{el} = 1$. While Hupp and Weaver [25] have considered various factors pertaining to κ_{el} , nevertheless, ignoring the tunneling probability *a priori* may not be justified either.

Recently a claim has been made [5] that λ_i could be neglected altogether in preference to an adjustment in pre-exponential term. The neglect of λ_i by these workers [5] is not justified. This also has, in a way, motivated us to investigate the role of λ_i in the calculation of k° for these pyridinium compounds.

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An un-substituted or methyl substituted pyridinium ion has only one center where an electron could go (at the N^+ center). A strong electron withdrawing substituent like CN, NO_2 , $COOCH_3$ etc. could affect the electron acceptability of N^+ center too [26]. This may be manifested in k^o , possibly through the variation in λ_i .

Standard heterogeneous electron transfer rate constant k^o is generally evaluated using DC voltammetry or AC polarographic technique [27]. Based on the theory of stationary electrode polarography on micro disk electrode, Nicholson [28], Gileadi [29], and Kochi [30] proposed methods for the determination of k^o and these have been used by many workers, however, the peak separation methods of Nicholson [28] have been the most popular [31-36]. However, there are inherent experimental problems, arising from the solution resistance and capacitance current. Besides, it was claimed by several workers that the use of micro size electrode in conjunction with the peak separation method gives lower k^o values [37]. Attention was thus turned to high speed voltammetry, at ultramicro electrode [37, and references therein].

The present study was carried out with the following purpose:

(i) Obtaining experimental k^o for some mono-cation pyridinium compounds. These pyridinium compounds (ions) being: *N*-methyl- α -Picolinium-(II), *N*-(2-4-dinitrophenyl)-4-(4'-pyridyl) pyridinium-(III), *N*-(phenyl)-4-(4'-pyridyl) pyridinium-(IV), *N*-(cyano-phenyl)-4-(4'-pyridyl) pyridinium-(V) and *N*-(2, 4) dinitrophenyl pyridinium-chlorides (VI). Whereas *N,N'*-dimethyl 4-4'-bipyridinium dichloride (methyl viologen dichloride) (I) was used as a reference compound. It may be noted that while literature is rich in the determination of k^o for reduction of neutral organic compounds, k^o 's for the reduction of cations, particularly pyridinium ion are scarce.

(ii) Analyzing the experimental k^o through Marcus equation and the so called modified Marcus equations.

(iii) Investigating the exponential factor of Marcus equation vis-a-vis the inclusion of inner-sphere organization energy λ_i .

An innovative (theoretical) study with regards to λ_i has been reported on 4-cyano-*N*-methyl pyridinium reduction [38]. However, reduction of

this compound is complicated by the formation of the methyl viologen cation radical [39].

(iv) Exploring the possibility of including diabaticity (nonadiabaticity) ($\kappa_{el} \neq 1$) in this system.

In the pyridinium compounds studied here, there are two types of substitution in the main pyridinium ion structure: at *N*-position and 4-position. Also there are strong electrons withdrawing groups. Their effect on redox properties [26] and k^o and hence on their electrochromic and nonlinear chromic properties [3-9] could also be of some interest.

Evaluation of Heterogeneous Electron Transfer Rate Constant k^o

Experimental k^o ($k^{\alpha, exp}$)

Experimental heterogeneous electron transfer rate constants ($k^{\alpha, exp}$) were obtained by cyclic voltammetric technique [27, 31] (see Experimental Section later) for a quasi reversible electrode process, according to Nicholson [28], $\Delta E_p [= (E_p)_c - (E_p)_a]$ is a function of v (scan rate), k^o , α , (transfer coefficient), and the switching potential, (E_s). The effect of switching potential is, however, negligible if the magnitude is at least 90/n mV beyond the cathodic peak. The heterogeneous rate constant k^o of the process is related to a function ψ which is related to ΔE_p . A table is given by Nicholson [28] relating ΔE_p and ψ . Thus through ΔE_p (at a particular scan rate) one obtains ψ and from ψ one obtains k^o , provided the diffusion coefficient of the substrate is known.

A simple but elegant method for the evaluation of k^o is due to Gileadi [29]. According to Gileadi method k^o is obtained from

$$k^o = -0.48\alpha + 0.52 + (\frac{1}{2}) \log [nFD\alpha V_c / (2.3 RT)] \quad (2)$$

where D , the diffusion coefficient, is in cm^2/s , V_c is the critical scan rate defined as the toe of E_p vs logarithm of the scan rate plot, α is the transfer coefficient and n is the number of electrons transferred.

Calculation of k^o ($k^{\alpha, calc}$): Marcus Equation

k^o is expressed in terms of "dynamical effect" *i.e.* pre-exponential term A and activation barrier effect *i.e.* exponential term ΔG^* (eq. (1)). These are briefly described below.

The Dynamical Effects

The pre-exponential term (or terms) has (have) been proposed to be

(a) collision frequency Z along with the electronic transmission coefficient κ_{el} . This term κ_{el} manifests the adiabaticity of an electron transfer reaction. For adiabatic reaction $\kappa_{el} = 1$. Thus

$$A = \kappa_{el} Z = Z \quad (3)$$

(b) The precursor equilibrium constant model where A is expressed in term of κ_{el} , a precursor equilibrium constant K_p and the effective nuclear frequency ν_n . Thus, [for example see Ref.17, 33, 40-42],

$$A = \kappa_{el} K_p \nu_n \quad (4)$$

where ν_n is related to longitudinal solvent relaxation time τ_L as [40-42]

$$\nu_n = \tau_L^{-1} (\lambda_o / 16 \pi RT)^{1/2} \quad (5)$$

τ_L is related to Debye relaxation time τ_D by.

$$\tau_L = (\bar{I} \ \nu / \epsilon_s) \tau_D \\ = 3 V_m \eta / RT; \quad V_m = M/\rho \quad (6)$$

ϵ_s , V_m and η are static dielectric constant, molar volume and viscosity of the solvent respectively $\bar{I} \ \nu$ is the dielectric constant at high frequency. Khan [43] has recommended

$$\nu_n = 1 / \tau_D \quad (7)$$

The Activation Barrier Effect: The Exponential Terms

In the exponential term (e.q. (1)), ΔG^* is the sum of outer and inner – organization energies. It is thus given by

$$\Delta G^* = \frac{\lambda_o + \lambda_i}{4} \quad (8)$$

where λ_o is the outer sphere re-organization and λ_i the inner sphere re-organization energy “barriers”. It is obvious that this exponential term is the one which has profound effect on k^o . A 10% variation in ΔG^* can affect the value of k^o as much as 100% variation

in the pre-exponential term A , hence the importance of λ_i .

Having said that, it is necessary to outline the various expressions for λ_o and λ_i (which are to be calculated)[see for example ref, 13,16-17],

$$\lambda_o = \{Ne^2 / (\epsilon_o 32 \pi)\} (1/a - 1/R_c) [1/\epsilon_{op} - 1/\epsilon_s] \quad (9)$$

where a is the radius of the substrate, R_c the distance from the image, and the expression in the bracket [] is Pekar parameter.

λ_i is a function of force constants f_j [44].

$$\lambda_i = \sum_j [(f_j \times f_j^*) / (f_j + f_j^*)] (\Delta q_j)^2 \quad (10)$$

The force constants of the reactant and product can be computed from the following relation – in molecular orbital (m.o.) prescription - [45].

$$f_j = B (1 + P_j) + c \quad (11)$$

$$f_j^* = B (1 + P_j^*) + c \quad (12)$$

P_j is given by

$$P_j = \sum_n C_{jm} C_{sm} \quad (13)$$

P_j is the bond order of J^{th} bond. C_{jm} are the coefficient of molecular orbitals. Under π -approximation M.O. prescription, the change in bond length Δq may be estimated via the bond-order-bond length relationship [45, 46].

$$\Delta q_j = D (P_j - P_j^*) \quad (14)$$

The value of coefficients D , B and c , (eqs. 11, 12, 14) in SCFMO prescription are $D = 0.18$ Angstrom (0.018 nm), $B = 9.85$ mdyne / Angstrom (= 9.85×10^2 N/nm) and $c = -9.445$ mdyne / Angstrom (= -9.44×10^2 N/nm) [15,31].

Some workers [23, 47-49] used m.o. calculation for the evaluation of λ_i , while some other [50, 51] used other methods.

Results and Discussion

There are two parts of this section.

1. Experimental k^o (= $k^{o, \text{exp}}$), and
2. Calculated k^o (= $k^{o, \text{calc}}$)

1. Experimental k^o ($= k^{o, \text{exp}}$)

As mentioned in the Experimental section (see later), measurements of $k^{o,s}$ ($k^{o, \text{exp}}$) were carried out in DMSO (0.1M TBAP). $k^{o, \text{exp}}$ for compounds I-VI as obtained by Nicholson and Gileadi methods [28, 29] are collected in Table-1.

Table-1: Experimental k^o , D_o and Z , ($T = 298 \text{ K}$).

Compound (radius, nm)	(Z cm/s)	$(k^o)_G^a$ $\times 10^3 \text{ cm/s}$	$(k^o)_N^b$ $\times 10^3 \text{ cm/s}$	$D_o \times 10^5 \text{ cm}^2/\text{s}$
MV ²⁺ I (0.55)	4601	42	54	1.9
MPC ⁺ II (0.38)	6038	5.6	2.2	0.93
DNPP ⁺ III (0.61)	3493	4.2	1.1	1.4
NPP ⁺ IV (0.57)	4112	6.6	1.3	0.85
NPCP ⁺ V (0.59)	3907	6.5	6.1	0.72
DNP ⁺ VI (0.57)	4002	1.9	4.2	0.98

(a) k^o as obtained by Gileadi method, (b) k^o as obtained by Nicholson method.

2. Calculated k^o ($= k^{o, \text{calc}}$)

It is noted that the various equations used for calculation of k^o , could be expressed in general form as eq. (1).

The scheme for calculations is given below.

Scheme for Calculations

Calculations were carried out according to the following Scheme.

- (a) $A = Z$ and $\Delta G^* = \lambda_o/4$ for $R_e = \infty$, $\kappa_{el} = 1$
 (b) $A = Z$, $\Delta G^* = (\lambda_o + \lambda_i)/4$ and $R_e = 2r$, $2(r + L)$ and ∞ , $\kappa_{el} = 1$, L is the radius of the solvent
 (c) $A = K_p V_n$ ($\kappa_{el} = 1$)

K_p = precursor constant taken as $6.0 \times 10^{-9} \text{ cm}$ (0.06nm) [51] (eq. 4), V_n calculated from eq (5) [$= 2.4 \times 10^{10} \text{ s}^{-1}$ at 25°C] and / or eq. (7) [$\tau_d = 2 \times 10^{-10} \text{ s}$ for DMSO]. ΔG^* was, as usual, taken as $(\lambda_o + \lambda_i) / 4$ for $R_e = 2r$, $2(r + L)$ and ∞ .

Calculation

- (a) Case $k^o = Z \kappa_{el} \exp [\Delta G^* / RT]$, $\kappa_{el} = 1$, $\Delta G^* = \lambda_o / 4$ for $R_e = \infty$.

Results of this most simple formula calculation are collected in Table-2. It is seen that the calculated values of k^o ($= k^{o, \text{calc}}$) under this prescription is way off from experimental $k^{o,s}$ (Table-1). While experimental $k^{o,s}$ are in the range of $10^{-3} - 10^{-2} \text{ cm}^2/\text{s}$, the calculated $k^{o,s}$ are in $10^n \text{ cm}^2/\text{s}$, $n \geq 0$, range. This formula, being inadequate, also necessitated improvement in calculation methodology / prescription.

Table-2^a: Calculated k^o : inclusion and exclusion of inner atmosphere re-organization energy λ_i , $T = 298 \text{ K}$.

Compound	λ_o^b (e.v)	$(k^o)_{2r}^b$ (cm/s)	$\lambda_o + \lambda_i^c$ (e.v)	$(k^o)_{2r+L}^c$	% λ_i/λ_o
I	0.575	17.1	0.6725	6.66	14.5
II	0.832	1.41	0.9014	0.94	7.7
III	0.516	23.0	1.184	0.035	56.4
IV	0.548	19.9	0.640	8.11	14.3
V	0.530	22.5	0.753	2.55	29.6
VI	0.558	17.6	1.173	0.043	52.6

(a) $k^o = \kappa_{el} Z \exp [-\Delta G^*/RT]$, $\kappa_{el} = 1$; (b) $\Delta G^* = \lambda_o/4$, λ_o for $R_e = \infty$; (c) $\lambda_i^{\text{SCF-UHF}}$.

(b) case $k^o = Z \kappa_{el} \exp [\Delta G^* / RT]$, $\kappa_{el} = 1$, $\Delta G^* = (\lambda_o + \lambda_i) / 4$ for $R_e = 2r$, $2(r + L)$ and ∞ . For DMSO $L = 0.6 \text{ nm}$ [36].

Results of the calculation are collected in Table-3.

Table-3^a: Calculated k^o with λ_o for $R_e = 2r$, $2(r + L)$, ∞ . The collision frequency model.

Compound	$k^{o,b}$ cm/s	$k^{o,c}$ cm/s	$k^{o,d}$ cm/s
I	6.66	25.2	108
II	0.94	4.4	15.3
III	0.035	0.121	0.42
IV	8.12	30.0	111.6
V	2.55	9.24	33.4
VI	0.043	0.163	0.660

(a) $k^o = \kappa_{el} Z \exp [-\Delta G^*/RT]$; $\Delta G^* = \frac{\lambda_i + \lambda_o}{4}$ (b) for λ_o for $R_e = \infty$,

(c) for λ_o for $R_e = 2(r + L)$ and (d) for λ_o for $R_e = 2r$.

When λ_i is included in ΔG^* , there is some improvement in calculated k^o in the sense that these calculated $k^{o, \text{calc}}$ (for λ_i included) are smaller in magnitude. In case of compounds III, V, and VI, there is a drastic reduction in the numerical values of calculated k^o (10 to 100 times reduction). It is also to be noted that in these compounds (III, V & VI) λ_i 's contributions to λ are 56.4%, 29.6% and 52.4%. Thus at least in these cases λ_i can not be ignored. Still it is noted that these calculated $k^{o,s}$ are still far higher than $k^{o, \text{exp}}$. Thus in all subsequent calculations of ΔG^* , λ_i is included. It may also be noted that the universal practice of ignoring λ_i in ΔG^* calculation if λ_i is less than 10% of λ seems to have some merit provided it is shown that $\lambda_i \leq 0.1\lambda$. which means λ_i 's should be evaluated any way before it can be dismissed. Evaluation of λ_i becomes even more important if comparisons are to be made between $k^{o,s}$ for first and second reduction processes [52]. It is noted that k^o calculated for λ_i for $R_e = 2r$ and $2(r + L)$, as expected, are much higher in magnitude.

- (c) Case $k^o = \kappa_{el} K_p V_n \exp [-\Delta G^* / RT]$

ΔG^* is again equal to $(\lambda_o + \lambda_i)/4$ and λ_o are for $R_e = 2r$, $2(r + L)$ and ∞ , $\kappa_{el} = 1$. K_p is precursor equilibrium constant. Values of various parameters have been described above (Scheme for calculations

(c). Results of these calculations are collected in Table-4. It is seen that the combination of $K_p = 6 \times 10^{-9}$ cm (0.06nm) and $v = 5 \times 10^{13} \text{ s}^{-1}$ (third column) gives k° 's which are way off compared to $k^{\circ, \text{exp}}$. May be κ_{cl} is not unity. From the fourth column of Table-4, it is seen that the combination of $K_p = 6 \times 10^{-9}$ cm (0.06 nm), and $v_n = 10^{10} \text{ s}^{-1}$ gives k° 's which are closer to the experimental values. However, best results in this model were obtained when $K_p = 6.0 \times 10^{-9}$ cm, $v_n = 5.0 \times 10^9 \text{ s}^{-1}$ and for ΔG^* (with $\lambda_o + \lambda_i$) when $R_c = \infty$ (Table-4, last column).

Table-4: Calculated k° using Precursor Model^a.

Compound	R_c	$k^{\circ, b}$ cm/s	$k^{\circ, c}$ cm/s	$k^{\circ, d}$ cm/s
I	2r	7.20×10^3	3.48	0.720
	2(r + L)	1.65×10^3	0.790	0.165
	∞	4.3×10^2	0.210	0.042
II	2r	7.6×10^2	0.38	0.075
	2(r + L)	2.28×10^2	0.108	0.023
	∞	4.80×10^1	0.024	0.005
III	2r	52.0	0.025	5.2×10^{-3}
	2(r + L)	10.5	0.018	1.02×10^{-3}
	∞	3.0	0.012	3.0×10^{-4}
IV	2r	8.4×10^3	4.03	0.84
	2(r + L)	2.2×10^3	1.05	0.22
	∞	4.2×10^2	0.29	0.06
V	2r	2.61×10^3	1.39	0.258
	2(r + L)	7.5×10^2	0.36	0.075
	∞	1.84×10^2	0.09	0.018
VI	2r	48	0.024	4.8×10^{-3}
	2(r + L)	12	0.006	1.2×10^{-3}
	∞	3	0.0015	3.0×10^{-4}

(a) $k^{\circ} = K_p V_n \exp[-\Delta G^*/RT]$, $\Delta G^* = (\lambda_o + \lambda_i)/4$, $K_p = 6.0 \times 10^{-9}$ cm,
 (b) $v_n = 5 \times 10^{13} \text{ s}^{-1}$ (c) $v_n = 2.4 \times 10^{10} \text{ s}^{-1}$ (d) $v_n = 1/\tau_d = 5.0 \times 10^9 \text{ s}^{-1}$ (eq(7))

While investigating potentiality of electrochromic property of compounds, workers have generally focused their attention on the redox potential of (potential) electrochromic substances. The present work, however aims to evaluate k° for potential electrochromic and nonlinear (electro)chromic pyridinium salts. These experimental k° were generally found to be low. On carrying out calculations it was found that some of these salts had quite high λ_i , which could have rendered k° quite low *i.e.* the electron transfer for these salts are sluggish hence unsuitable for electrochromic devices compared to viologens (ref. Table-1).

Because the change in solvent is a convenient way to investigate the solvent dynamics *vis a vis*, the electron transfer process, manifested through k° , most workers in the field of electron transfer process have paid their attention to this (solvent dynamics) aspect of electron transfer and not on λ_i [See e.g. 19-22, 40-48].

Generally low values of k° are looked with suspicion, particularly if k° has been evaluated

through Nicholson method. The low k° is suspected to be due to IR problem. Very high values of k° are also not above suspicion, particularly if recorded on solid electrodes. It has been shown that k° is related to fractal parameters of a solid electrode, which means, the surface condition including pores and grooves [53] affect k° . These parameters are rarely reported alongside k° 's obtained on solid electrodes.

Disregarding instrumental or any other artifacts being the cause of low k° values, attempts have been made here to explain them through Marcus theory [10, 23, 33, 48] through considering the exponential and the pre-exponential terms (of Marcus equation). What causes low value of k° , can thus be investigated.

Exponential Term

First the exponential factor is discussed here. The exponential term contains two terms λ_o and λ_i . Being in exponent, a slight variation in these parameters can have more profound effect than the variation in pre-exponential terms. λ_o in the simpler formula, contains the radius of the substrate, the distance from image forces (R_c) and the Peker parameters. In λ_o , the variable parameters are R_c and the dielectric constant (ϵ_s) of the solvent. For studies on various compounds in a single solvent ϵ_s is constant as in the present case. It is then R_c which can influence λ_o . R_c is taken as 2r, 2(r + L) and ∞ , where r is the radius of the substrates and L for the solvent, here DMSO, is 0.6 nm [36]. From the calculated values of $k^{0, \text{calc}}$ for all these values of R_c (Tables 3-5), the lowest values of $k^{0, \text{calc}}$ are obtained for $R_c = \infty$. Thus in the present case (low $k^{\circ, \text{exp}}$) it might be tempting to confine the calculation to $R_c = \infty$, as has been recommended by some workers too [5, 10, 33, 48]. The other parameters in ΔG^* is λ_i , the inner re-organization energy the present case, in some pyridinium compounds (III & VI) λ_i 's are quite high. This affects the calculated values of standard heterogeneous electron transfer rate constant ($k^{0, \text{calc}}$) by reducing its numerical value (Table-2 compare k° for λ_o and k° for $\lambda_o + \lambda_i$ for compounds [III & VI]).

Some comments are needed about the existence of quite high λ_i values, particularly for compounds III & VI (compound V also has relatively higher λ_i value). It may be noted these λ_i 's have been calculated through HF / UHF - SCF - molecular orbital calculations in pi-orbital approximation, hence no drastic changes in molecular geometry could be expected or inferred.

Table-5: k^o calculated using Khan Model^a.

Compound	$k^o \times 10^3$ (cm/s) for δ (nm)	0.85	0.75	0.65	0.60	0.55
Re						
I	2r	0.670	3.58	19.3	45.7	110
	2(r + L)	0.190	1.02	5.54	13.1	31.6
	∞	0.060	0.310	1.67	3.94	9.51
II	2r	0.12	0.61	3.32	7.85	18.9
	2(r + L)	0.01	0.06	0.35	0.83	2.02
	∞	0.0075	0.04	0.220	0.510	1.23
III	2r	0.0033	1.70	9.40	22.2	5370
	2(r + L)	0.0012	0.61	3.30	7.8	1890
	∞	0.0004	0.20	1.10	4.0	610
IV	2r	0.79	4.20	22.7	53.7	5370
	2(r + L)	0.25	1.33	7.17	16.9	1890
	∞	0.08	0.41	2.23	5.28	610
V	2r	0.27	1.26	6.79	16.0	38.7
	2(r + L)	0.08	0.42	2.28	5.40	13.0
	∞	0.030	0.140	0.730	1.73	4.16
VI	2r	0.005	0.025	0.13	0.31	0.76
	2(r + L)	0.0014	0.008	0.04	0.095	0.23
	∞	0.0004	0.002	0.012	0.024	0.07

(a) The pre-exponential factors $A = \kappa_{el} \delta v_n$, when $\nu = \tau_L^{-1} [\lambda_o/16 \pi RT]^{1/2}$;

$$\tau_L = \left(\frac{\epsilon_\infty}{\epsilon_s} \right) \tau_D; \kappa_{el} = \exp [-0.804 \delta U_m^{1/2}]; \text{ and } U_m = \Phi_m - 36.0/\epsilon_{op} \delta$$

(see Ref. 43; where $\Phi_m = 4.53$ eV for Hg electrode, $\epsilon_{op} = 2.1747$ for DMSO

Grampp [48] has reported a wide variation in λ_i 's in various compounds, ranging from 11.0 kJ/mol to 45.3 kJ/mol. Hale [23] had reported λ_i ranging from 2.40 kJ/mol for anthracene to 60 kJ/mol for cyclo-octatetraen (however, the case of cyclo-octatetraene is a special case). These varied values of λ_i indicate that λ_i values depend upon the nature (geometry/structure), the substituent in the substrate molecules as well as how it (λ_i) is calculated (the m.o method, geometry optimization *etc*).

In the present study HF/UHF-SCF MO calculation in pi-orbital approximation was carried out hence geometry of the ions studied is fixed as planar. However, it is noted that the three compounds III, V & VI have strong electron withdrawing (electrophore) group - (di-) nitro and cyano. These groups have quite high Hammett sigma-values (for nitro: $\sigma^+ = 0.79$, for cyano = 0.66). It is possible that these groups compete with the main pyridinium ring as electron transfer sites, thus affecting the coefficients of atomic orbitals, which in turn affects the calculated bond orders (force constant) and displacement parameters Δq (eqs. 10-14). The other explanation could be that in compounds III, V & VI more normal coordinates are involved in the inner reorganization energy.

Pre-Exponential Term A

In the present studies two main models were used.

- (i) $A = \kappa_{el} Z$ ($\kappa_{el} = 1$), the classical model, and

- (ii) $A = \kappa_{el} K_p v_n$ ($\kappa_{el} = 1$) the precursor model, in vogue these days.

It is noted (Tables-2 and 3) that using model (i) *i.e.* classical model, $k^{o, calc}$ is nowhere near the $k^{o, exp}$. Thus model (i) is to be discarded and (ii) is to be considered. In using model (ii) with K_p , the dimension of which being cm, a manifestation of distance, a value of 6×10^{-9} cm (0.06nm) has been advocated [19-20]. This value may be taken as the lower limit of the distance since for lower distances, van der Waal or other forces, not accommodated in Marcus theory may complicate the scenario. At 0.5nm distance, the contribution of van der Waal energy is 0.002 eV [54]. After fixing the value of $K_p = 6 \times 10^{-9}$ cm, the other variable left is v_n (κ_{el} assumed to be unity). It is noted that $v_n = [O] 10^{10} s^{-1}$ gives reasonable k^o values. $v_n = 10^{13} s^{-1}$ has been used by some workers [48-49] but it gives too high values of k^o in the present case (see Table-4). The best agreement, between $k^{o, calcd}$ and $k^{o, expt}$, under precursor model, however, is found when $v_n = 5.0 \times 10^9 s^{-1}$ [43], which implies the simple eq.(7) is preferred.

This section will not be complete without discussing an alternative, interesting nevertheless pertinent and useful model – the Khan model [43] – of heterogeneous electron transfer reaction.

Khan [43] model, in which κ_{el} may not be assumed to be unity, proposes that:

$$A = \kappa_{el} \delta v_n \quad (15)$$

where δ , a new term, is the distance between the electrode and the reaction plane, OHP (Outer Hemmhottz Plane). Khan gives a simple expression for the evaluation of κ_{el}

$$\kappa_{el} = \exp [-0.804 \delta U_m^{1/2}] \quad (16)$$

where $U_m = \Phi_m - 36.0 / (\epsilon_{op} \delta)$; Φ_m is the work function, here 4.53 e.v. for the mercury electrode, and U_m is interfacial potential-energy barrier maximum.

Generally $\delta \geq r$, where r is the radius of the substrate. Khan model was selected particularly because it gives a simple expression for calculating κ_{el} .

This Khan model has, apparently, three variable κ_{el} , δ and v_n . Values of v_n could be fixed as in the precursor model *i.e.* $v_n = [O] 10^{10} s^{-1}$. κ_{el} depends upon δ , the distance parameters, so here also after fixing the value of v_n , only one parameter is

variable, that is δ . A range of δ value was used, but here $\delta = 6.0 (\pm 0.5) \times 10^{-10}$ m seems to give reasonable k^0 values (Table-5).

Khan's model and the precursor model both are acceptable but under Khan model, the electron transfer may not necessarily be taken as adiabatic.

Experimental

Standard heterogeneous electron transfer rate constant k^0 (cm s^{-1}) was determined measuring peak potentials, their peak separation $\Delta E_p = E_p^a - E_p^c$ and using Nicholson [28] and Gileadi [29] methods, E_p 's and ΔE_p 's as function of scan rate were determined from voltammogram scanned at low and high scan rates.

Instrumentation, Chemical and Procedure

Instrumentation, chemicals and procedure used in evaluating k^0 have been described before [3-4, 31-32] but it is summarized here. Concentration of electrolyte, tetra n- butylammonium perchlorate was 0.1M. The solvent, dimethyl sulfoxide (DMSO) was purified as per literature [55]. Nitrogen was purified by passing stream of nitrogen through traps containing vanadous sulfate, chromium chloride-zinc amalgam and the solvent DMSO. Concentration of the substrate was in 1-5 mM range.

EG&G PAR Polarographic Analyzer 174 A and X-Y Recorder (RE0074) were used for low scan measurement while potentiostat (PAR model 173) with

Coulometer (PAR Model 179), Universal Programmer (PAR model 175) in conjunction with storage oscilloscope (Textronic model 5103N) with plug in modules 5A20 and 5B10N were used for high scan measurements. A LAUDA thermostat (model K-4R) was used for maintaining constant temperature during measurement (25°C). A SCE was used as reference electrode. A salt bridge (PAR K0065) DMSO / 0.5 MTBAP was used to avoid contamination of the solution and poisoning of the electrode. All pyridinium compounds, (*N*-methly-4-picolinium-(II); *N*-(2,4-dinitrophenyl)-4-(4'-pyridyl) pyridinium-(III); *N*-(phenyl)-4-(4'-pyridyl) pyridinium-(IV); *N*-(cyanophenyl)-4-(4'-pyridyl)pyridinium- (V); and *N*-(2,4-dinitrophenyl) pyridinium-chlorides. (VI), were gifts from ICI Cheshire, Runcorn. U.K and was used without further purification. Methyl viologen (I) was also gift from ICI. Methyl viologen from Sigma gave the same result as the one from ICI.

Evaluation (Reliability) of k^{expt} , Various Factors

The procedure and the basis for the evaluation of k^0 have been described in references [56, 31-32].

In experimentally determining k^0 , various factors which affect its value are to be noted and taken care of. These factors are (i) (uncompensated) resistance of solution (the IR problem), (ii) approximation(s) incorporated in the particular (Nicholson / Gileadi) methods and (iii) adsorption. The last mentioned factor, adsorption, was not encountered in the present investigation. In general the uncompensated ohmic resistance poses problem, sometime serious. However, using three-electrode system with the reference electrode in the near proximity of the working electrode, use of high dielectric constant solvent and high salt concentration minimizes the error due to uncompensated resistance. In the present study these three measures were operative; the salt bridge of the SCE was placed within few mm from the working electrode, DMSO has high dielectric constant ($\epsilon_s = 47$) and the salt concentration in solution being 0.1M. Nevertheless two approaches were made to assess the intensity of the error in the measurement of k^0 . These being (a) estimating the $i_p R$ (i_p = peak current) and (b) using a reference compound whose k^0 has been reported before. For later purpose methyl viologen (*N*, *N*-dimethyl bipyridinium dichloride) was used.

Coming to (a), i_p for planar electrode is given by (for $n = 1$)

$$i_p = 0.4463 FA C_o^b \sqrt{D_o a} \quad (17)$$

For r = radius of Hg drop = 0.5 mm, $D_o = 1 \times 10^{-5} \text{ cm}^2/\text{s}$, $C_o^b = 1\text{mM}$, scan rate 1.0V/s, temperature 298 K and $R = 100 \Omega$ [58], $i_p R = [O]$ 1 mV; [O] means order of.

For Gileadi method there is an error of 1.0 mV at 1.0V/s scan rate while for Nicholson method, it would be twice. This is one of the reasons Gileadi method is preferred for k^0 measurement.

Now to (b), as mentioned above MV^{2+} was used as a references material. Diffusion coefficient of MV^{2+}/MV^+ and k^0 for $MV^{2+} + e = MV^+$ have been reported earlier. D_o was $6.0 \times 10^{-6} \text{ cm}^2/\text{s}$ in $\text{H}_2\text{O} + \text{THF} / \text{LiClO}_4$ system [57] and $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$ in DMF / 0.1M TBAP system [15, 58]. In the present case D was obtained as $1.9 \times 10^{-5} \text{ cm}^2/\text{s}$ (in DMSO / 0.1M TBAP) which is close to the previous reported values. k^0 as reported previously being $2.1 \times 10^{-2} \text{ cm/s}$

in THF+H₂O/LiClO₄ [58] and 2.4×10^{-2} cm/s in DMF / O.1M.TBAP system [13]. k° in the present study was obtained as 4.2×10^{-2} cm/s. (Table-1, Gileadi method) and 5.4×10^{-2} cm/s (Nicholson method, Table-1) in DMSO / 0.1M TBAP system.

These values are also close to the previously reported values. Thus the rate constants obtained for other five pyridinium compounds should be reliable. In the present study k° for $MV^{2+} \rightarrow MV^{+}$ was also determined in DMF/O.1M TBAP system. The value was 0.023 cm/s which is quite close to the previously reported values as mentioned above.

Conclusion

From the studies on the e-transfer involving pyridinium compounds, it is concluded that λ_i can not be neglected; rather λ_i should be evaluated, particularly when strong electron withdrawing substituents are present near the site (of electron transfer) in the substrate. High calculated λ_i values correlate qualitatively with the electron withdrawing power of the substituent. It is also inferred that according to precursor model $\kappa_{el} < 1$, (i.e. the systems being nonadiabatic), is not important in the present case. Khan model, however, indicates that the non-adiabaticity (i.e. diabaticity) in electron transfer process involving pyridinium ions is important, except for picolinium ion, where the radius is less than 0.5 nm. This finding is rather surprising: One would expect tunneling through narrow barrier (small radius, closer approach) rather than broad barrier (larger radius, farther away from the electrode), larger pyridinium ions. An important inference of this study is that when a strong electron withdrawing substituent is near reaction site, λ_i will be quite high.

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